DAY

The Devitrification of Glass

Chemical Engineering

B. S.

1913

THE DEVITRIFICATION OF GLASS

BY

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

1913

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June 4, 1913.

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Phillmer Wymond Day

ENTITLED The Devitrification of Glass

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

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THE DEVITRIFICATION OF GLASS.

INTRODUCTION.

Glass making is one of the oldest of the industries. None being older unless it is that of brick making. In fact, both were made for the first time at such an early date that there is no definite knowledge as to where, how, or when their methods of manufacture were first discovered. According to Pliny, glass was first discovered by the Phoenicians. They supported some cooking utensils on the sand with blocks of soda. From the heat of the fire the soda and sand fused together forming glass. This, however, is very improbable since it is not likely that under such conditions a sufficiently high temperature would be obtained to fuse the glass.

The only positive evidence that we have of the earliest glass making is some relics found in Egypt. Archaelogists have discovered sculptured designs representing glass blowers at work giving evidence that glass making was an industry as far back as 4000 B.C.

The advancement made up to the present time in the manufacture of art glass is not as far ahead of that attained by the ancient Egyptians as might be apparent. Imitations of precious stones have been found in the old Egyptian tombs. Glass made into difficult shapes and of various colors has also been discovered.

As nearly as can be learned the manufacture of glass continued until the overthrow of the Roman Empire by the barbarians of Northern Europe. During the succeeding Dark ages only one phase of the glass industry (the making of stained glass) was continued.

It was only at the beginning of the nineteenth century that glass making began to thrive again. From that time until the present day, it has advanced until now it is becoming one of the great industries.'

According to Bizer, glass is a transparent solid formed by the fusion of siliceous and alkaline matter, which assumed while passing through sand a state of fusion a temperature sufficiently high, a fluid condition, and, as the temperature falls, passing from the fluid through a ductile viscous state to a solid - devoid of crystalline structure, impenetrable to both gases and liquid. fluids - a hard, brittle mass which exhibits when broken, a lustrous fracture.

According to the more modern and scientific definition, glass is not a solid but a super-cooled liquid. It is a well known fact to the physical chemist that a solution, when cooled quickly and without agitation, can be cooled to a temperature many degrees below its freezing point without crystallization. This same principle applies to glass. When at a high temperature or in the liquid state it is no more than a solution of its severally combined constituents. As it is cooled it becomes more viscous and when it reaches ordinary temperatures it becomes rigid, a "congealed liquid". Glass when melted does not become liquid at any definite temperature but as the temperature increases it becomes less viscous. This also would tend to indicate that it was not a solid, since, according to definition, a solid must have a definite melting point.

If glass which has been cooled quickly is again heated to a temperature near its softening point, and held at that temperature

for a period of time and then allowed to cool slowly crystallization will take place. The amount of velocity of crystallization varying with the composition of the glass, the temperature at which it was heated, the time of heating, and the rate of cooling. This phenomenon is known as devitrification.

Glasses high in SiO_2 are more liable to devitrify than those low in SiO_2 and This is due to crystallization out of the excess component SiO_2.

The composition of glass is varied according to various physical and chemical properties desired in the finished product. The general formula for a glass is

$$\left.\begin{array}{l} y\ Na_2O \\ z\ CaO \end{array}\right\} x\ SiO_2 \ ,$$

where Na_2O varies from 0 to 1, the CaO varies from 1 to 0, the SiO_2 varies from 1 to 5 and y + z equals one. The physical properties of the glass may be varied by a change in the ratio of these constituents or by the substitution of some other base for the Na_2O or the CaO. A decrease in lime with an increase in Na_2O lowers the temperature of fusion and decreases the resistance to chemical reagents. An increase in lime with a decrease in the Na_2O increases the resistance to chemical reagents, elasticity, hardness, tendency to devitrify, index of refraction, and an increase in the temperature of fusion. K_2O may be substituted for Na_2O giving a clearer, more brilliant, and more easily fusible glass, but more expensive. K_2O finds its use in the higher grades of glass.

Glasses of a higher specific gravity may be obtained by substituting a base of higher molecular weight for one of lower molecular weight. For example PbO is used in many glasses as a

substitute for CaO, especially in optical glasses. The specific gravity increases as the PbO increases. In optical glasses a high index of refraction is required and neither hardness or resistance to chemical reagents is of primary importance.

A great many other oxides are used in the glass batch but the per cent is usually small. They are used only for special kinds of glass or coloring effects desired in different glasses, or as decolorizing agents.

By far the most expensive constituent in the more common grades of glass is soda and the cheapest constituent is the SiO_2. An increase in SiO_2 increases the tendency to devitrify and also increases the temperature of fusion. Therefore the use of SiO_2 is limited on account of the devitrification in annealing and cost of fuel to fuse the batch.

The more uptodate bottle factories are now using machines for making most of their ware. The tendency for the machine-made bottle to devitrify is increased, since during the process of shaping it is kept at a high temperature longer than the hand made bottiel. In order to obtain as good a product it is necessary to use a glass which will not devitrify so easily. This can be done by increasing the amount of soda or adding a small,amount of Al_2O_3. An increase in soda increases the cost of the batch to such an extent that it would cut down the profits. The addition of Al_2O_3 according to many glass makers increases the temperature of fusion which will also add to the cost of the product.

This experimental investigation is divided into two parts, The object of the first part is to find out the effect of Al_2O_3 on devitrification. The object of the secont part is to get some idea

of the relative fusion temperature of glasses that vary in SiO_2 and Al_2O_3. Since glass has no definite melting point, the relative fusion or softening temperatures are determined by measuring the viscosity changes in the glass at variously increasing temperatures.

EXPERIMENTAL INVESTIGATION.

PART I.

In order to test the effect of Al_2O_3. Devitrification of soda lime. Glasses. Experiments were begun in October, 1913, under the direction of Mr. Stull, head of the Ceramics Department at the University of Illinois.

First a series of glass batches were made up according to the following formulae,

$$\left.\begin{array}{l} .4\ Na_2O \\ .6\ CaO \end{array}\right\} x\ SiO_2.$$ The SiO_2 varying from 2 to 5 mols., each member of the series differing by .3 of a mol.

A very pure finely ground flint was used as the source of the SiO_2. The source of the CaO was a whiting obtained in the Laboratory of the Ceramics Department, which was practically pure $CaCO_3$. The soda was a commercial grade of Na_2CO_3, which was also practically pure Na_2CO_3. These raw materials were ground to pass through a twenty mesh sieve, weighed out, and mixed in the following proportions.

First member. I - 1.

$$\left.\begin{array}{l} .4\ Na_2O \\ .6\ CaO \end{array}\right\} 2\ SiO_2.$$

Wt. Na_2O calculated to Na_2CO_3.
Wt. CaO " " $CaCO_3$.

Na_2O = 62	Na_2CO_3 = 106.	.4 Na_2CO_3 = 42.4
CaO = 56.09	$CaCO_3$ = 100.9	.6 $CaCO_3$ = 60.034
SiO_2 = 60.3		2 SiO_2 = 120.6

In order to get a batch of approximately 600 grams the weights were

multiplied by 3.

$$42.4 \times 3 = 127.2$$

$$60.054 \times 3 = 180.16$$

$$120.6 \times 3 = 361.8$$

Percentage composition of glass, calculated from batch weights assuming that there is no volatilization other than expulsion of CO_2, and that the raw materials are pure.

Na_2O	- 13.83 per cent	=	24.8
CaO	- 18.78 per cent	=	33.6
SiO_2	- 67.39 per cent	=	120.6

Second member. I - 2.

$$\left.\begin{array}{l} .4\ Na_2O \\ .6\ PbO \end{array}\right\} 2.3\ SiO_2$$

Batch weight.

Na_2CO_3	=	127.32
$CaCO_3$	=	180.16
SiO_2	=	416.06 grams.

Percentage composition.

24.8	=	Na_2O	=	12.58
33.6	=	CaO	=	17.02
138.8	=	SiO_2	=	70.40

Third member. I - 3.

Batch weight.

$$\left.\begin{array}{l} .4\ Na_2O \\ .6\ CaO \end{array}\right\} 2.6\ SiO_2.$$

M_2CO_3	=	127.32
$CaCO_3$	=	180.16
SiO_2	=	470.00

Percentage Composition.

24.8	=	Na_2O	=	11.54 per cent.
33.6	=	CaO	=	15.62 per cent.
156.6	=	SiO_2	=	72.84 per cent.
215.0				

Fourth Member. I - 4.

$$\left.\begin{array}{l} .4\ Na_2O \\ .6\ CaO \end{array}\right\} 2.9\ SiO_2.$$

Batch weight.

Na_2CO_3 = 127.32
$CaCO_3$ = 180.16
SiO_2 = 525.04

Percentage Composition.

.4 Na_2O	=	24.8	=	10.64 per cent.
.6 CaO	=	33.6	=	14.44 per cent.
2.9 SiO_2	=	174.8	=	74.92 per cent.
		233.2		

Fifth member. I - 5.

Batch weight.

$$\left.\begin{array}{l} .4\ Na_2O \\ .6\ CaO \end{array}\right\} 3.2\ SiO_2.$$

Na_2CO_3 = 127.32
$CaCO_3$ = 180.16
SiO_2 = 580.00

Percentage Composition.

.4 Na_2O	=	24.8	=	9.87 per cent.
.6 CaO	=	33.6	=	13.38 per cent.
3.2 SiO_2	=	193.0	=	76.85 per cent.
		251.4		

Sizth member. I - 6.

Batch weight.

$$\left.\begin{array}{l} .4\ Na_2O \\ .6\ CaO \end{array}\right\} 3.5\ SiO_2.$$

Na_2CO_3 = 127.32
$CaCO_3$ = 180.16
SiO_2 = 634.00

Percentage Composition.

.4 Na_2O	=	24.8	=	9.20 per cent.
.6 CaO	=	33.6	=	12.49 per cent.
3.5 SiO_2	=	211.2		78.30 per cent.

Seventh member. I - 7

Batch weight.

$$.4\ Na_2O \\ .6\ CaO \Big)\ 3.8\ SiO_2.$$

Na_2CO_3 = 127.32
$CaCO_3$ = 180.16
SiO_2 = 687.00

Percentage Composition.

.4 Na_2O	= 24.8	= 8.63	per cent.
.6 CaO	= 33.6	=11.70	per cent.
3.8 SiO_2	= 229.0	=79.67	per cent.
	287.4		

Eighth member. I - 8.

Batch weight.

$$.4\ NaO \\ .6\ CaO \Big)\ 4.1\ SiO_2.$$

Na_2CO_3 = 127.32
$CaCO_3$ = 180.16
SiO_2 = 741.06

Percentage Composition.

.4 Na_2O	= 24.8	# 8.12	per cent.
.6 CaO	= 33.6	= 11.00	per cent.
4.1 SiO_2	= 247.0	= 80.88	per cent.
	305.4		

Ninth member. I - 9.

Batch weight.

$$.4\ Na_2O \\ .6\ CaO \Big)\ 4.4\ SiO_2.$$

Na_2CO_3 = 127.32
$CaCO_3$ = 180.16
SiO_2 = 795.0

Percentage Composition.

.4 Na_2O	= 24.8	= 7.66	per cent.
.6 CaO	= 33.6	= 10.44	per cent.
4.4 SiO_2	= 265.4	= 81.94	per cent.
	323.8		

Tenth member. I - 10

Batch weight.

$$\left.\begin{matrix} .4\ Na_2O \\ .6\ CaO \end{matrix}\right)\ 4.7\ SiO_2$$

Na_2CO_3	=	127.32
$CaCO_3$	=	180.16
SiO_2	=	849.00

Percentage Composition.

.4 Na_2O	=	24.8	=	7.26 per cent.
.6 CaO	=	33.6	=	9.84 per cent.
4.7 SiO_2	=	281.4	=	82.90 per cent.
		340.8		

Eleventh member. I - 11.

Batch weight.

$$\left.\begin{matrix} .4\ Na_2O \\ .6\ CaO \end{matrix}\right)\ 5\ SiO_2.$$

Na_2CO_3	=	127.32
$CaCO_3$	=	180.16
SiO_2	=	904.5

Percentage Composition.

.4 Na_2O	=	24.8	=	6.90 per cent.
.6 CaO	=	33.6	=	9.33 per cent.
5.0 SiO_2	=	301.5	=	83.77 per cent.
		359.9		

These batches were mixed and ground in the Ball mills for three hours in order to obtain an intimate mixture of the constituents.

The glasses were fused in small port furnace, using Denver fire clay crucibles as containers. The fusion was continued until a clear glass was obtained though it was not entirely free from bubbles.

An attempt was first made to form small plates of glass by rolling the molten glass on an inor plate with a small steel roller. This was found impossible since the glass in such small quantities cooled so quickly that it became hard before it could

be worked. The test pieces of clear glass were obtained by pouring the molten glass on a small steel plate and allowing it to cool gradually in a small furnace.

Test pieces of the first five members of the series were obtained without much trouble. In fusing the sixth member of the series, the crucible vitrified before a clear glass was obtained. The Denver fire clay crucible was the only one that could be obtained in the department at this time, consequently a more refractory crucible was made. The batch weight of crucible body was as follows:

Mt. Savage Flint Clay	=	10.lbs.
Grog.	=	30.
St.Louis Plastic Fire	=	12.
Cutter's ball clay	=	12.
Na_2CO_3	=	0.05

The Mt. Savage Flint Clay was crushed and screened to 40 mech. The grog was crushed and screened to forty mesh and washed on a 100 mesh sieve. That which remained on the 100 mesh being used for the body. The St. Louis plastic fire clay, ball clay, and the Ba_2CO_3 were weighed and ground in a ball mill to consistency. To this slip were added the flint clay and the grog, the mixture of which was pugged on a plaster slab to a plastic moulding consistency.

Two plaster moulds were made and the crucibles formed on a pigger wheel.

The crucibles were dried for ten days and then burned to Seger cone 8 (1290° C.) in one of the new kilns of the Department of Ceramics.

These crucibles proved to be refractory enough but cracked

when the glass was fused in them. In order to obtain a more fusible series of glasses which could be worked more advantageously at lower temperatures a new set was made up according to the following plan.

The first series correspond to the formula -

$$\left.\begin{matrix} .6\ Na_2O \\ .4\ CaO \end{matrix}\right\}\ x\ SiO_2.$$

The SiO_2 varying from 2.75 to 3.75. The numbers of the series being II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-8, II-9.

The second series was made up according to the formula,

$$\left.\begin{matrix} .6\ Na_2O \\ .4\ CaO \\ \end{matrix}\right\}\ \begin{matrix} .05\ Al_2O_3 \\ x\ SiO_2. \end{matrix}$$

The SiO_2 varying from 3.25 to 3.75. The numbers of the series being III-5, III-6, III-7, III-8, and III-9. It was considered unnecessary to make up members of the series containing Al_2O_3 with less SiO_2 since according to Mr. Gelathary, a glass of the formula

$$\left.\begin{matrix} .2\ MgO \\ .2\ CaO \\ .6\ Na_2O \end{matrix}\right\}\ 3.13\ SiO_2,$$

devitrifies under favorable conditions.

One member of another series of the following formula was made -

$$\left.\begin{matrix} .6\ Na_2O \\ .4\ CaO \end{matrix}\right\}\ \begin{matrix} .1\ Al_2O_3 \\ 3.375\ SiO_2. \end{matrix}$$

This one was made in order to get an idea of the effect of an increase in Al_2O_3.

The members of these three series were weighed out and mixed as follows -

First member. II - 1.

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right)\ 2.75\ SiO_2$$

Batch weight.

Na_2CO_3 = 140.48
$CaCO_3$ = 120.12
SiO_2 = 498.00

Percentage composition of resulting glass, assuming that raw materials are pure and no volatilization takes place during the fusion other than the expulsion of CO_2.

.6 Na_2O	=	37.2	=	16.54 per cent.
.4 CaO	=	22.4	=	9.96 per cent.
2.75 SiO_2	=	165.5	=	73.50 per cent.
		225.1		

Second member. II - 2.

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right)\ 2.875\ SiO_2$$

Batch weight.

Na_2CO_3 = 190.98
$CaCO_3$ = 120.12
SiO_2 = 520.70

Percentage Composition.

.6 Na_2O	=	37.2	=	15.97 per cent.
.4 CaO	=	22.4	=	9.53 per cent.
2.875 SiO_2	=	173.0	=	74.50 per cent.
		232.6		

Third member. II-3.

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right)\ 3.\ SiO_2.$$

Batch weight.

Na_2CO_3 = 190.98
$CaCO_3$ = 120.12
SiO_2 = 343.3

Percentage Composition.

.6 Na_2O	=	37.2	=	15.46 per cent.
.4 CaO	=	22.4	=	9.29 per cent.
3.0 SiO_2	=	180.9	=	75.25 per cent.
		240.5		

Fourth member. II - 4

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right\} 3.125\ SiO_2.$$

Batch weight.

Na_2CO_3 = 190.98
$CaCO_3$ = 120.12
SiO_2 = 566.20

Percentage composition.

.6 Na_2O	= 37.2	=	15.01 per cent.
.4 CaO	= 22.4	=	9.04 per cent.
3.125 SiO_2	= 188.3	=	75.95 per cent.
	247.9		

Fifth member. II - 5.

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right\} 3.25\ SiO_2.$$

Batch weight.

Na_2CO_3 = 190.98
$CaCO_3$ = 120.12
SiO_2 = 588.90

Percentage composition.

.6 Na_2O	= 37.2	=	14.56 per cent.
.4 CaO	= 22.4	=	8.77 per cent.
3.25 SiO_2	= 195.8	=	76.67 per cent.
	255.4		

Sixth member. II - 6.

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right\} 3.375\ SiO_2.$$

Batch weight.

Na_2CO_3 = 190.98
$CaCO_3$ = 120.12
SiO_2 = 611.60

Percentage composition.

.6 Na_2O	= 37.2	=	14.16 per cent.
.4 CaO	= 22.4	=	8.52 per cent.
3.375 SiO_2	= 203.0	=	77.32 per cent.
	262.6		

Seventh member.

Formula. II - 7.

$$\left.\begin{array}{l}.6\ Na_2O \\ .4\ CaO\end{array}\right\}\ 3.5\ SiO_2.$$

Na_2CO_3	=	190.98
$CaCO_3$	=	120.12
SiO_2	=	636.2

Percentage Composition.

.6 Na_2O	=	37.2	=	13.78 per cent.
.4 CaO	=	22.4	=	8.28 per cent.
3.5 SiO_2	=	<u>211.0</u>	=	77.94 per cent.
		270.6		

Eighth member. II - 8.

Formula. Batch weight.

$$\left.\begin{array}{l}.6\ Na_2O \\ .4\ CaO\end{array}\right\}\ 3.625\ SiO_2.$$

Na_2CO_3	=	190.98
$CaCO_3$	=	120.12
SiO_2	=	656.20

Percentage Composition.

.6 Na_2O	=	37.2	=	13.33 per cent.
.4 CaO	=	22.4	=	8.04 per cent.
3.625 SiO_2	=	<u>219.0</u>	=	78.63 per cent.
		278.6		

Ninth member. II - 9.

Formula. Batch weight.

$$\left.\begin{array}{l}.6\ Na_2O \\ .4\ CaO\end{array}\right\}\ 3.75\ SiO_2.$$

Na_2CO_3	=	190.98
$CaCO_3$	=	120.12
SiO_2	=	679.5

Percentage composition.

.6 Na_2O	=	37.2	=	13.00 per cent.
.4 CaO	=	22.4	=	7.84 per cent.
3.75 SiO_2	=	<u>225.8</u>	=	79.16 per cent.
		285.4		

Tenth member. III - 5.

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right\} \begin{array}{l} .05\ Al_2O_3. \\ 3.25\ SiO_2. \end{array}$$

Batch weight.

Na_2CO_3 = 190.98
$CaCO_3$ = 120.12
SiO_2 = 588.90
$Al(OH)_3$ = 23.4

Percentage Composition.

.6 Na_2O	=	37.2	=	14.24 per cent.
.4 CaO	=	22.4	=	8.58 per cent.
3.25 SiO_2	=	195.8	=	75.62 per cent.
.05 Al_2O_3	=	5.11	=	.96 per cent.
		260.51		

Eleventh member. III - 6.

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right\} \begin{array}{l} .05\ Al_2O_3 \\ 2.375\ SiO_2 \end{array}$$

Batch weight.

Na_2CO_3 = 190.98
$CaCO_3$ = 120.12
SiO_2 = 611.60
$Al(OH)_3$ = 23.4

Percentage Composition.

.6 Na_2O	=	37.2	=	13.92 per cent.
.4 CaO	=	22.4	=	8.38 per cent.
3.375 SiO_2	=	203.0	=	75.78 per cent.
.05 Al_2O_3	=	5.11	=	1.92 per cent.
		267.71		

Twelfth member. III - 7.

Formula.

$$\left.\begin{array}{l} .6\ Na_2O \\ .4\ CaO \end{array}\right\} \begin{array}{l} .05\ Al_2O_3 \\ 3.5\ SiO_2 \end{array}$$

Batch weight.

Na_2CO_3 = 190.98
$CaCO_3$ = 120.12
SiO_2 = 626.20
$Al(OH)_3$ = 23.4

Percentage Composition.

.6 Na_2O	=	37.2	=	13.52 per cent.
.4 CaO	=	22.4	=	8.12 per cent.
3.5 SiO_2	=	211.0	=	76.50 per cent.
.05 Al_2O_3	=	5.11	=	1.86 per cent.
		275.71		

III - 8.

Formula.

$.6\ Na_2O$)
($.05\ Al_2O_3$
$.4\ CaO$) $3.625\ SiO_2$

Batch weight.

$Na_2CO_3 = 190.98$
$C4CO_3 = 120.12$
$SiO_2 = 656.20$
$Al(OH)_3 = 23.40$

Percentage Composition.

$.6\ Na_2O$	= 37.2	=	13.10	per cent.
$.4\ CaO$	= 22.4	=	7.90	per cent.
$3.625\ SiO_2$	= 219.0	=	77.20	per cent.
$.05\ Al_2O_3$	= 5.11	=	1.80	per cent.
	283.71			

III - 9.

Formula.

$.6\ Na_2O$)
($.05\ Al_2O_3$
$.4\ CaO$) $3.75\ SiO_2$.

Batch weight.

$Na_2CO_3 = 190.98$
$CaCO_3 = 120.12$
$SiO_2 = 679.5$
$Al(OH)_3 = 23.4$

Percentage Composition.

$.6\ Na_2O$	= 37.2	=	12.79	per cent.
$.4\ CaO$	= 22.4	=	7.75	per cent.
$3.75\ SiO_2$	= 225.8	=	77.70	per cent.
$.05\ Al_2O_3$	= 5.11	=	1.76	per cent.
	290.51			

IV - 6.

Formula.

$.6\ Na_2O$)
($.1\ Al_2O_3$
$.4\ CaO$) $3.375\ SiO_2$.

Batch weight.

$Na_2CO_3 = 190.98$
$CaCO_3 = 120.12$
$SiO_2 = 611.60$
$Al(OH)_3 = 46.88$

Percentage Composition.

$.6\ Na_2O$	= 37.2	=	13.56	per cent.
$.4\ CaO$	= 22.4	=	8.21	per cent.
$3.375\ SiO_2$	= 203.0	=	74.48	per cent.
$.1\ Al_2O_3$	= 10.22	=	3.75	per cent.
	272.82			

These glasses proved more fusible than the first series made up. Test pieces were obtained as described under the first series, of the following members: II-1, II-2, II-3, II-4, II-5, II-6, II-7, II-7, II-9, III-5, III-6, III-7, III-8, III-9, and IV-6.

The last one, IV-6, was so viscous on account of the high content of Al_2O_3 that it was almost impossible to pour.

These test pieces were annealed by heating to a temperature of 550° C. for two hours and allowing to cool slowly. When cold, none of these showed any signs of devitrification.

These same pieces were then heated at a temperature of 700° C. for three hours and again allowed to cool slowly. When cold these test pieces which did not contain Al_2O_3 had become porcelain white in appearance, showing that devitrification had taken place, while thosecontaining Al_2O_3 were not affected.

EXPERIMENTAL INVESTIGATION.

PART II.

In order to obtain some data on the relative fusion or softening temperatures of the different glasses made in the first part of the investigations an apparatus was arranged as shown in Fig.I, The crucibles used were of the following composition:

8 per cent Spar.
22 per cent Ball Clay.
30 per cent Calcined Kaolin.
40 per cent SiO_2.

A batch was weighed out according to the above and ground in a ball mill for five hours with sufficient water to make a slop suitable for casting. The crucibles were made by casting them in plaster molds and after drying were burned to 1200° C. in a small pot furnace.

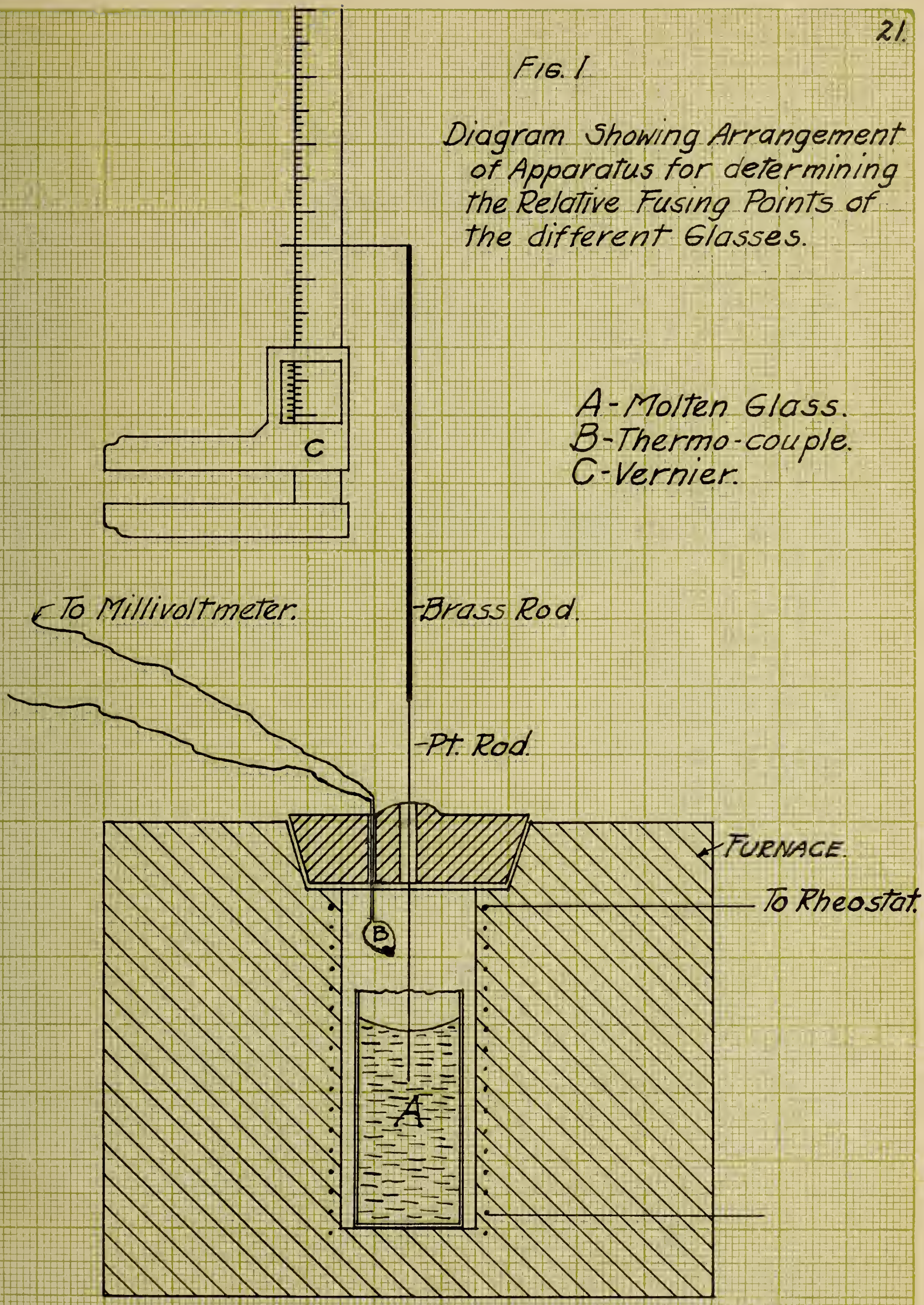
In these crucibles glasses of each of the following members were tested: II-2, II-3, II-4, II-5, II-6. II-7, II-8, II-9, III-6, III-7, III-8, III-9, and IV-6. A sufficient amount of the glass to nearly fill the crucible was fused and then allowed to cool, forming a smooth surface. The crucible containing the cooled glass was placed in the furnace and the platinum rod weighing 8.745 grams allowed to rest on the surface as shown in Fig.I. By the use of a rheostat the temperature was increased according to the time-temperature curve. Fig.II.

At intervals of one minute readings of the temperature and the vernier were taken. From the data obtained in this manner

curves 1 to 13 inclusive were plotted using the temperature in degrees Centigrade as absciassae and the distance in tenths of mm.as ordinates. Curve 14 was plotted using the temperature at which the rod had sunk 12 mm. below the surface, as abscissae and using moles SiO_2 in glasses II-2 to II-9 as ordinates. Curve 15 was plotted using the temperature at which the rod had sunk 12 mm. below the surface as absciaase and the mols SiO_2 in glass III-6 to III-9 as ordinates. Curve 16 was plotted using the temperatuure at which the rod had sunk 12 mm. below the surface as abscissae and Moles Al_2O_3 in glasses II-6, III-6, and IV-6, as ordinates.

Fig. I

Diagram Showing Arrangement of Apparatus for determining the Relative Fusing Points of the different Glasses.



A - Molten Glass.
B - Thermo-couple.
C - Vernier.

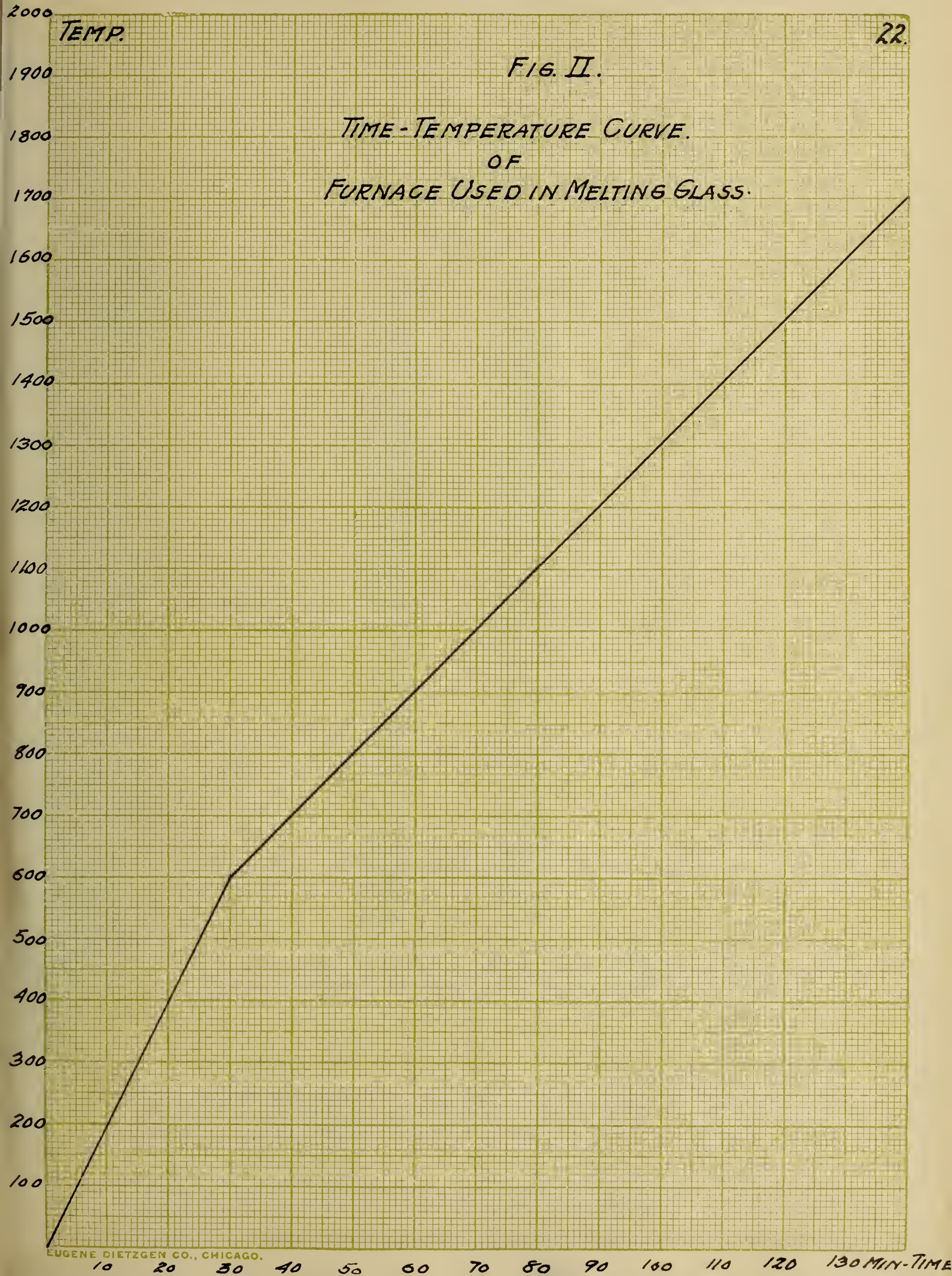
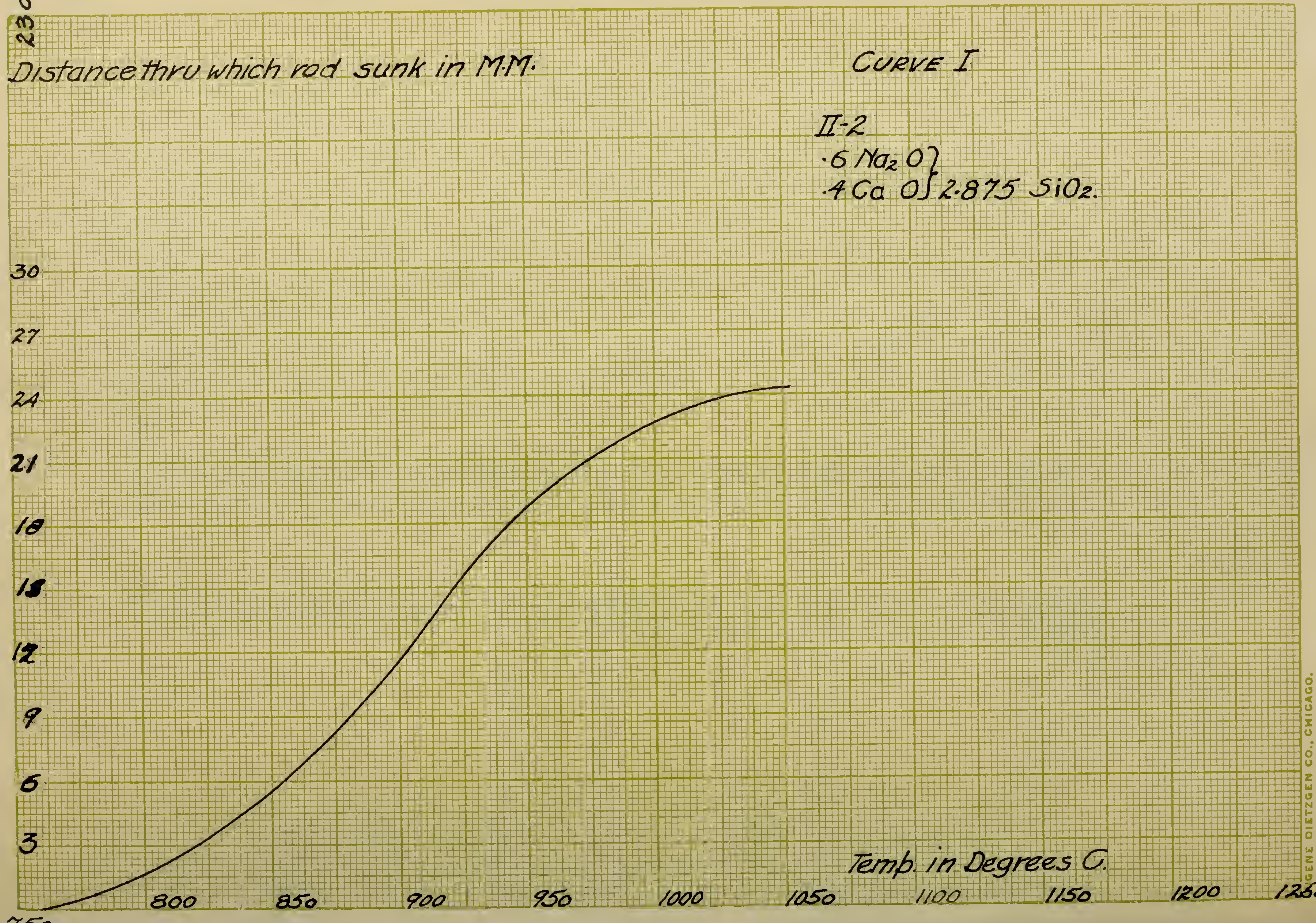


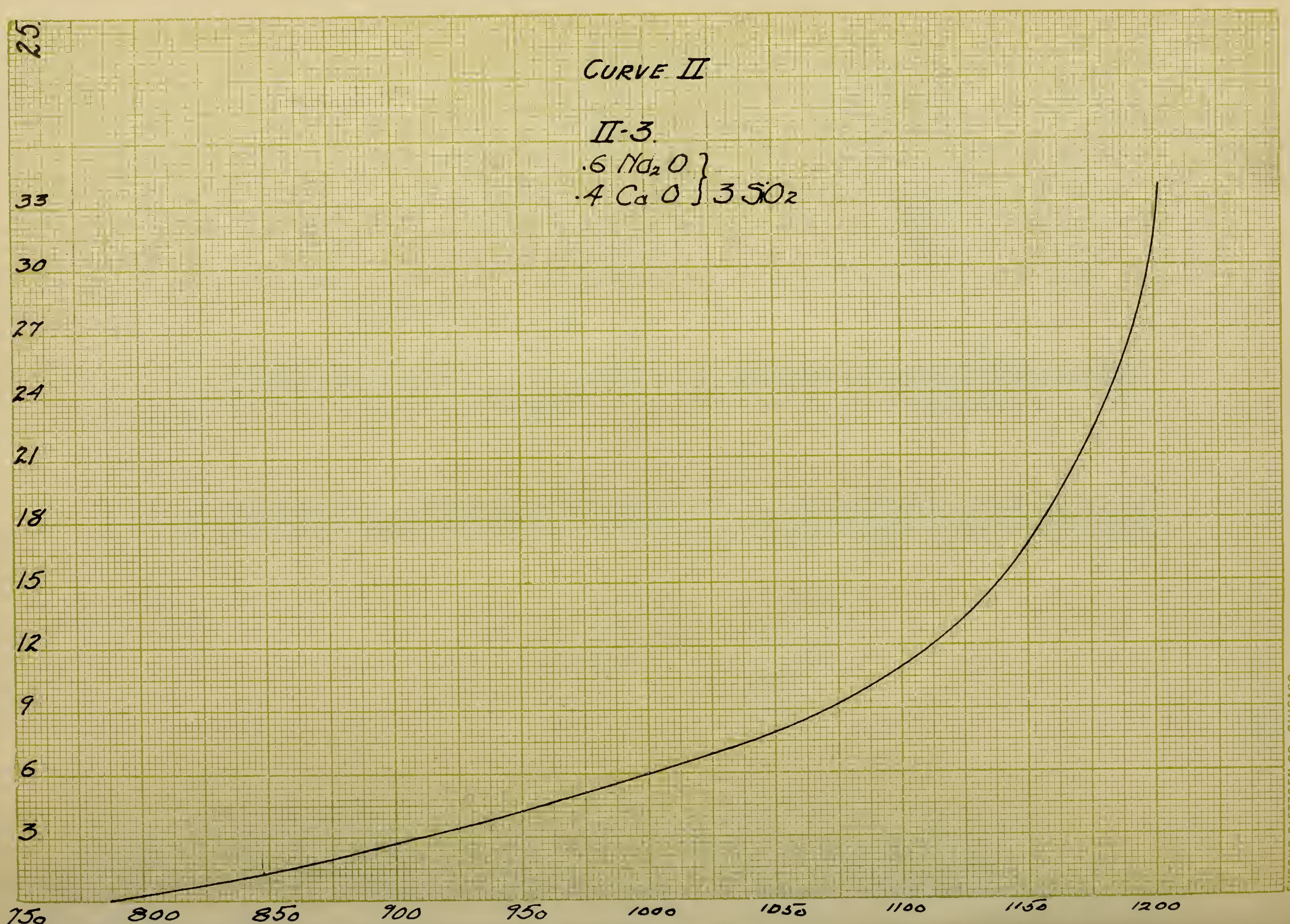
FIG. II.

TIME-TEMPERATURE CURVE. OF FURNACE USED IN MELTING GLASS.

II - 2.

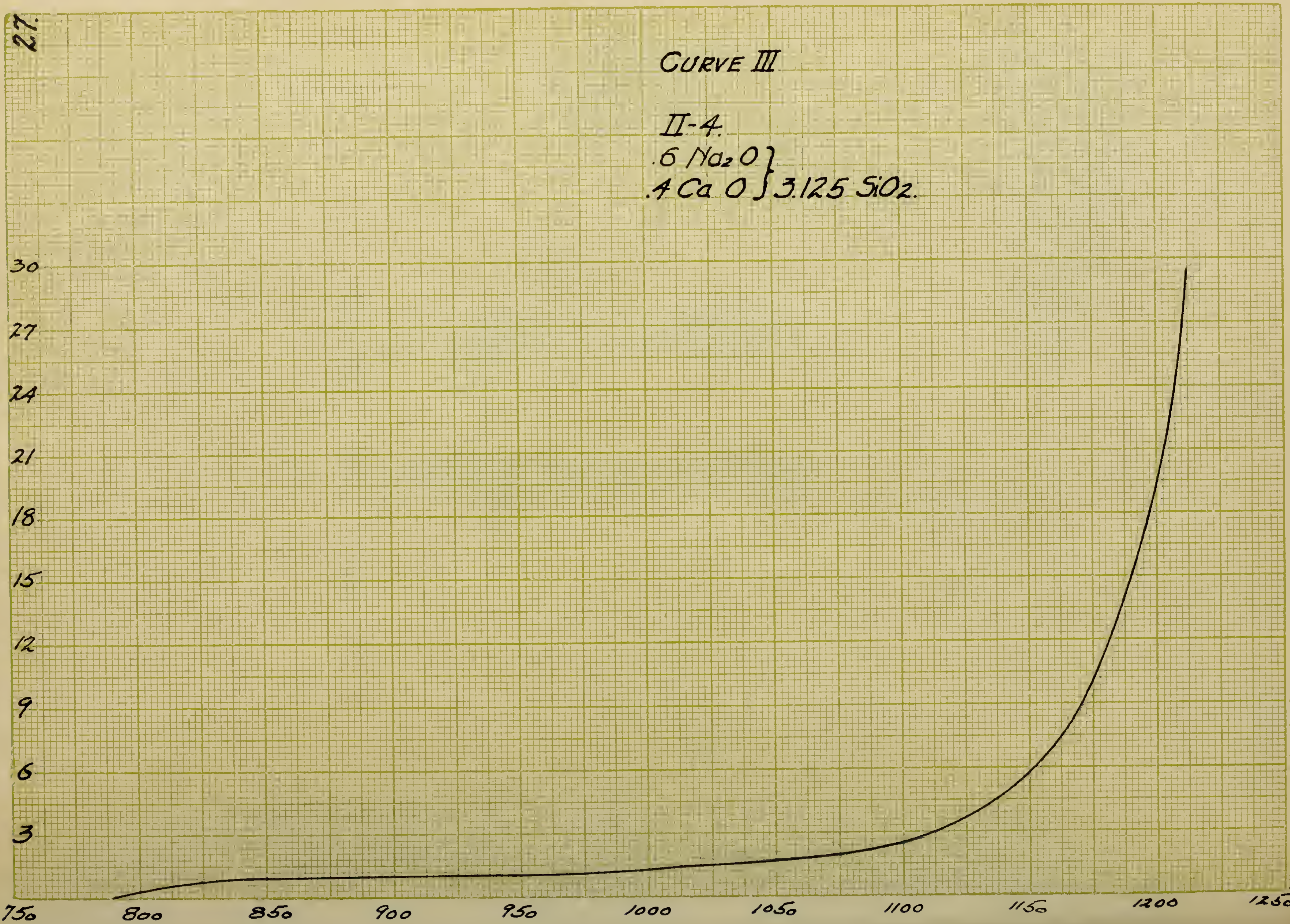
Time.	Temp.	Vernier.
	770	5:73
	780	5:70
	790	5:65
	800	5:62
	810	5:55
	820	5:50
	830	5:27
	840	5:16
	850	5:05
	860	----
	870	5:00
	880	4:87
	890	4:70
	900	4:56
	910	4:40
	920	4:24
	930	4:08
	940	3:94
	950	3:85
	960	3:76
	970	3:68
	980	3:60
	990	3:52
	1000	3:46
	1010	3:40
	1020	3:37
	1030	3:34
	1040	3:31
	1050	3:30


Distance thru which rod sunk in M.M.
Curve I
II-2
·6 Na2 O
·4 Ca O 2·875 SiO2.
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
Temp. in Degrees C.
GENE DIETZGEN CO., CHICAGO.


CURVE II
II-3.
.6 Na₂O
.4 CaO
3 SiO₂
3
6
9
12
15
18
21
24
27
30
33
750
800
850
900
950
1000
1050
1100
1150
1200
EUGENE DIETZGEN CO., CHICAGO.

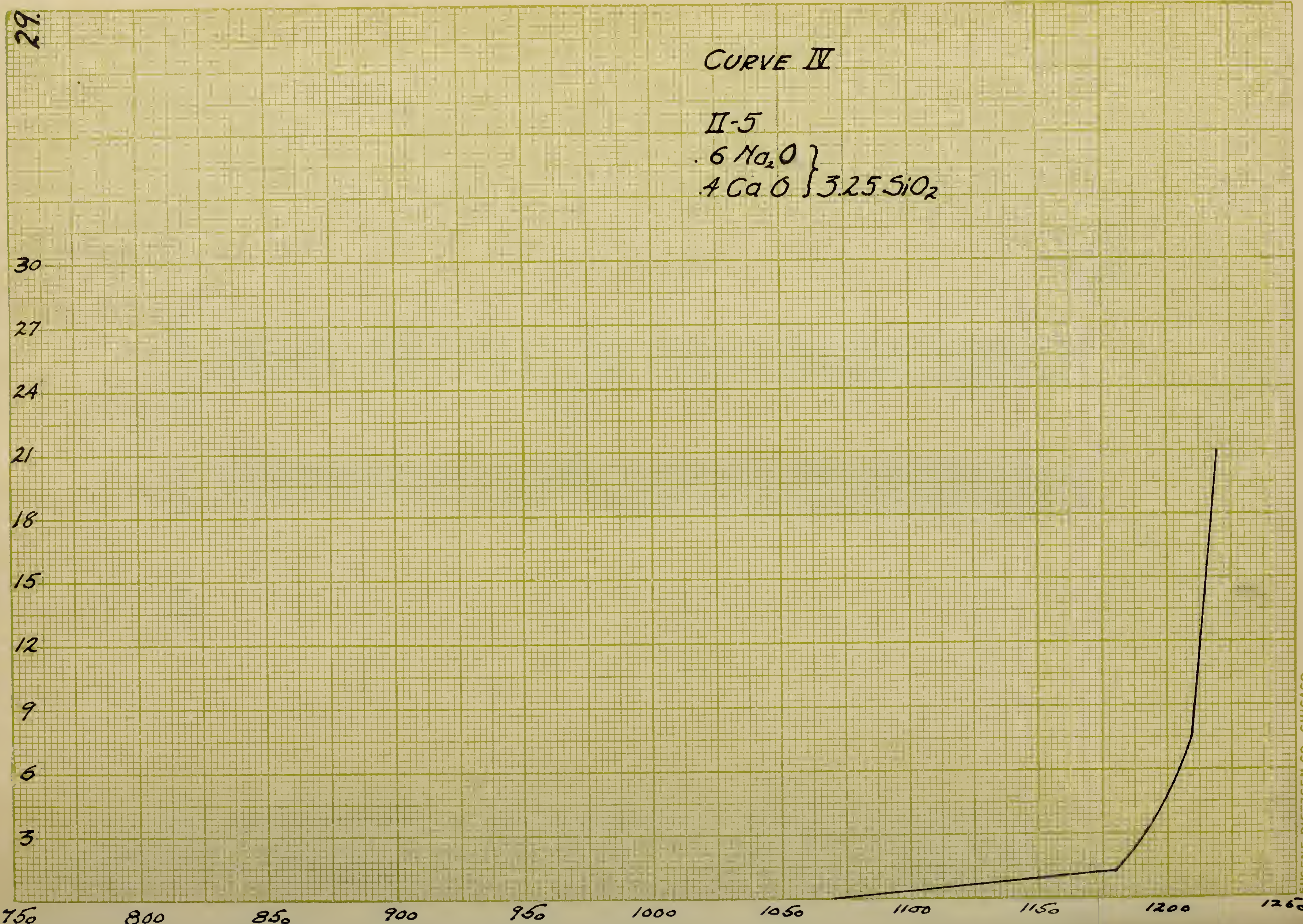
II - 4.

Time.	Temp.	Vernier.
	790	6:00
	800	5:99
	810	5:96
	820	5÷95
	830	----
	840	5:92
	850	----
	860	----
	870	5.90
	880	----
	890	----
	900	----
	910	----
	920	----
	930	----
	940	----
	950	----
	960	----
	970	----
	980	5.88
	990	----
	1000	----
	1010	5.86
	1020	----
	1030	5.85
	1040	5.84
	1050	5.83
	1060	5.82
	1070	----
	1080	5.80
	1090	5.78
	1100	5.74
	1110	5.76
	1120	5.65
	1130	5.57
	1140	5:55
	1150	5:42
	1160	5:30
	1170	5:13
	1180	4:84
	1190	4:46
	1200	4:00
	1210	3:34
	1220	----


CURVE III
II-4.
.6 Na2O
.4 CaO
3.125 SiO2.
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
EUGENE DIETZGEN CO., CHICAGO.

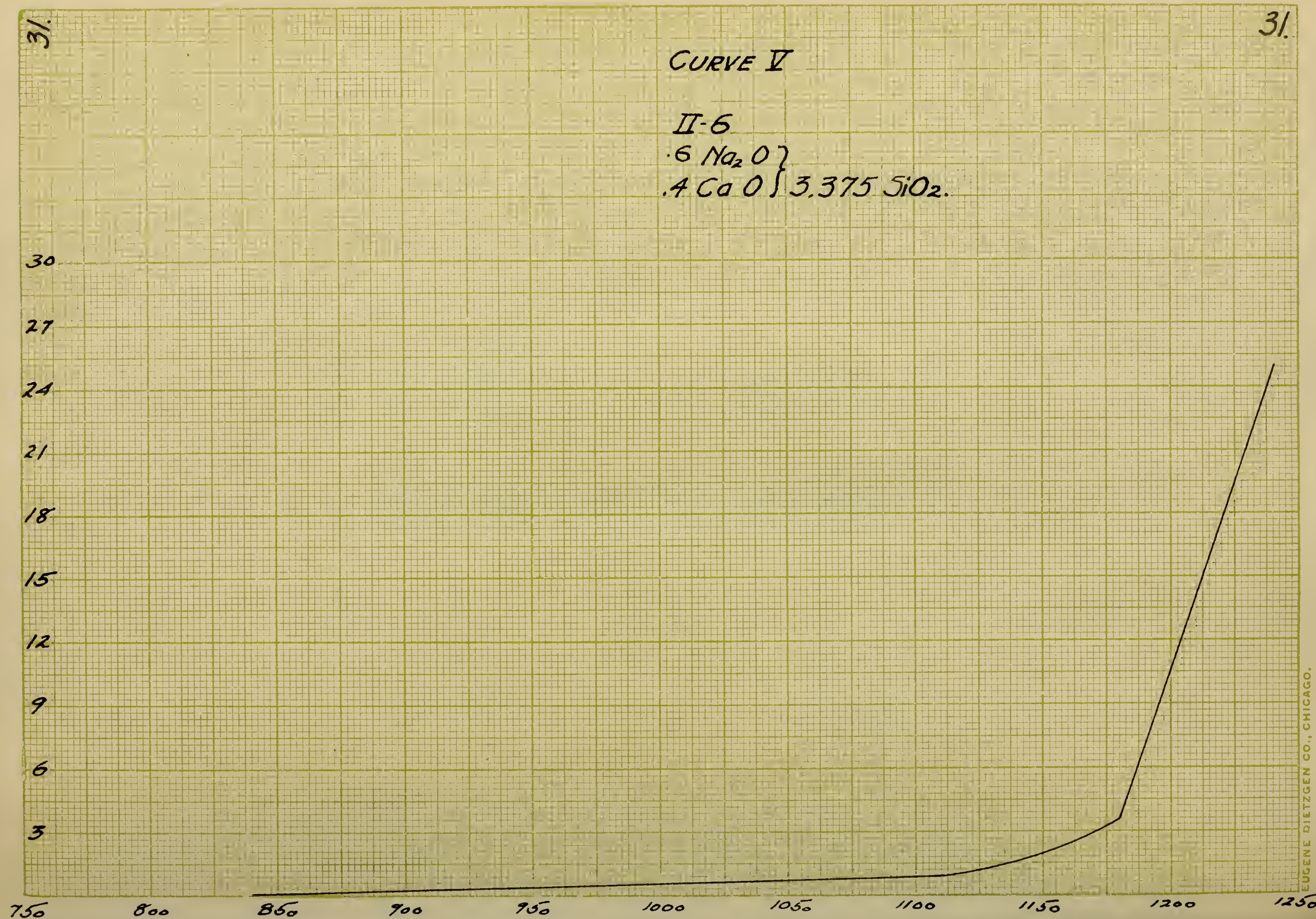
II - 5.

Time.	Temp.	Vernier.
	1040	5:70
	1050	----
	1060	----
	1070	----
	1080	5:68
	1090	----
	1100	5:67
	1110	5:65
	1120	----
	1130	----
	1140	----
	1150	----
	1160	----
	1170	----
	1180	5:58
	1190	5:45
	1200	5:24
	1210	4:94
	1220	3:70
	1230	----


CURVE IV
II-5
.6 Na_2O
.4 CaO
3.25 SiO_2
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1260
EUGENE DIETZGEN CO., CHICAGO.

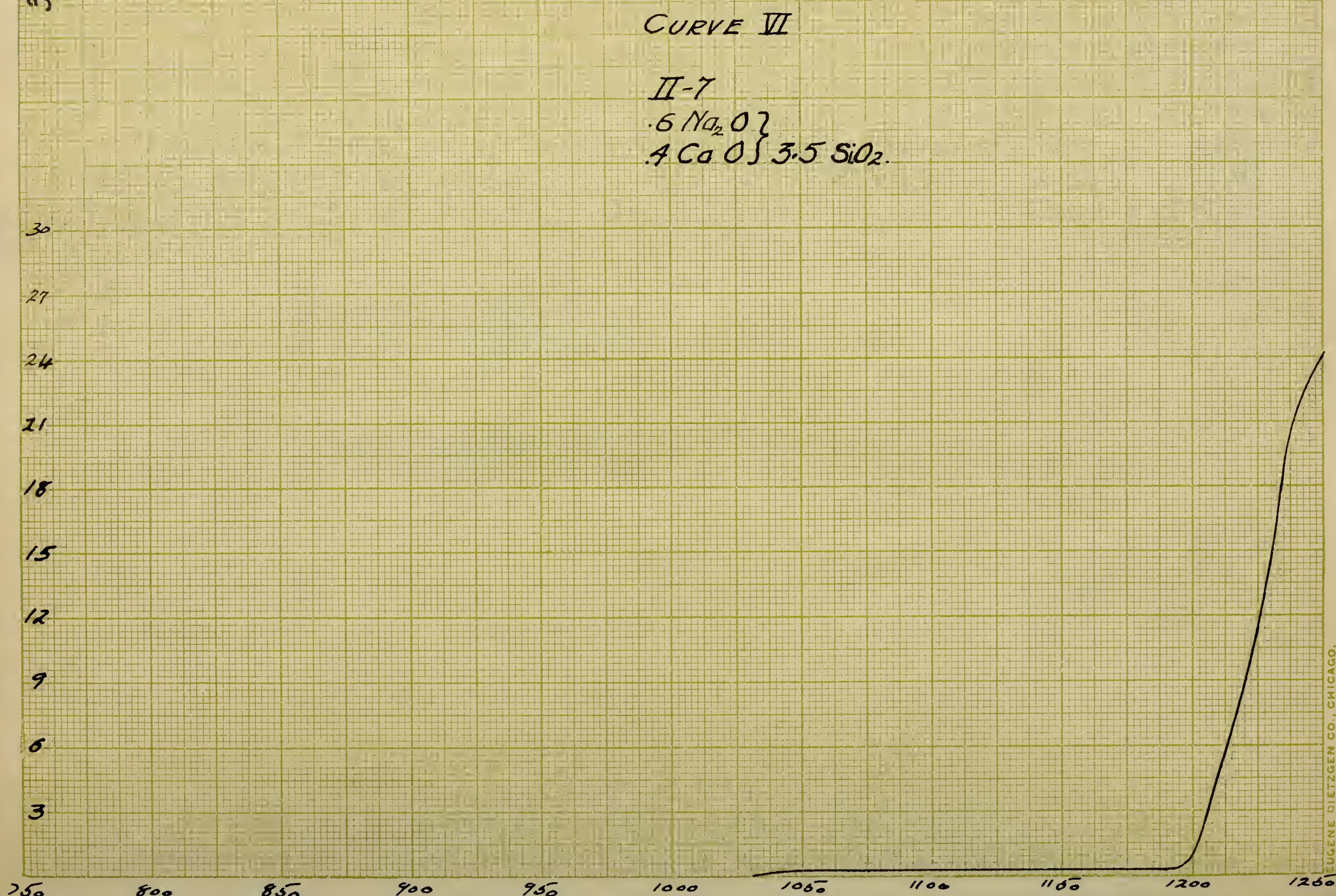
II - 6.

Time.	Temp.	Vernier.
	850	5:85
	860	5:84
	870	5:83
	880	----
	890	5:82
	900	----
	910	----
	920	----
	930	5:81
	940	----
	950	----
	960	----
	970	----
	980	----
	990	----
	1000	----
	1010	-----
	1020	5:80
	1030	----
	1040	----
	1050	5:79
	1060	5:78
	1070	5:77
	1080	----
	1090	----
	1100	----
	1110	5:76
	11120	----
	1130	5:70
	1140	5:67
	1150	5:64
	1160	5:60
	1170	5:55
	1180	5:48
	1190	5:13
	1200	4:81
	1210	4:52
	1220	4:20
	1230	3:72
	1240	3:35
	1250	----


31.
31.
CURVE V
II-6
.6 Na2O
.4 CaO 3.375 SiO2.
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
EUGENE DIETZGEN CO., CHICAGO.

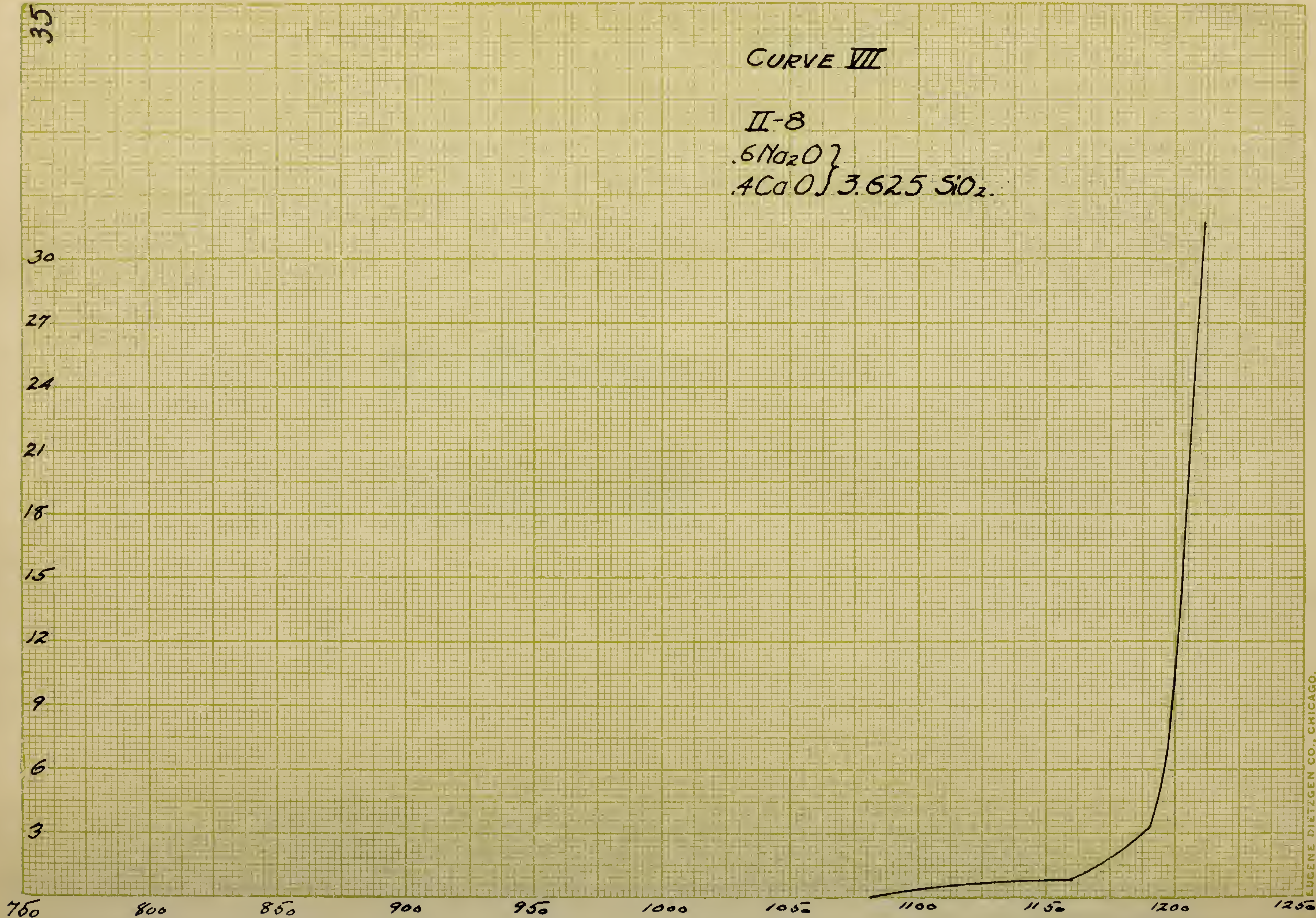
II - 7.

Time.	Temp.	Vernier.
	1030	6:05
	1040	6:03
	1050	----
	1060	----
	1070	----
	1080	----
	1090	----
	1100	----
	1110	----
	1120	----
	1130	----
	1140	----
	1150	----
	1160	----
	1170	----
	1180	----
	1190	----
	1200	5:95
	1210	5:56
	1220	5:15
	1230	4:58
	1240	3:84
	1250	3:04
	1260	----


CURVE VII
II-7
.6 Na_2O
.4 CaO 3.5 SiO_2.
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
EUGENE DIETZGEN CO., CHICAGO.

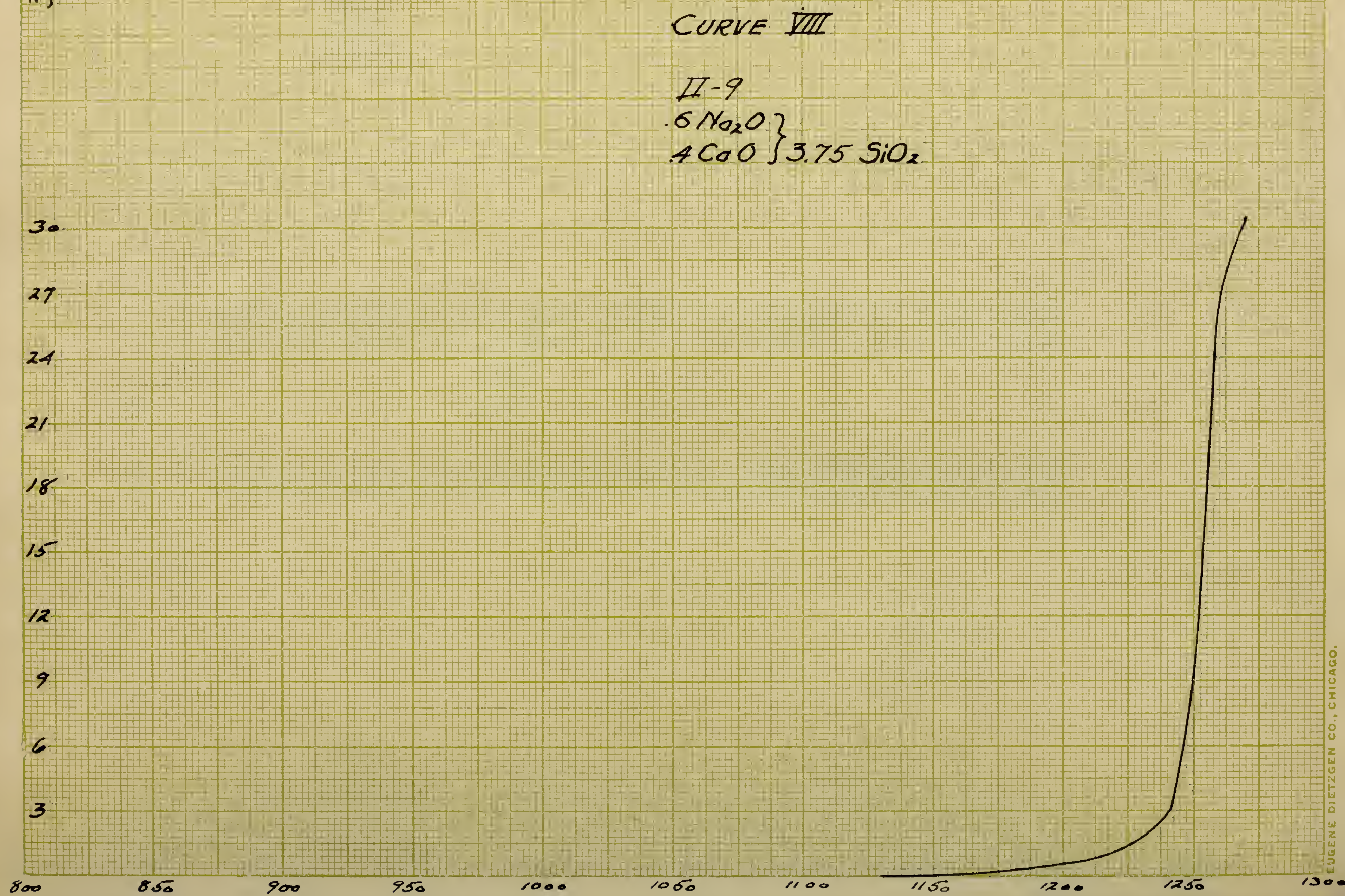
II - 8.

Time.	Temp.	Vernier.
	1130	6:79
	1140	6:78
	1150	6:77
	1160	6:76
	1170	6:74
	1180	----
	1190	----
	1200	6:73
	1210	6:71
	1220	6:64
	1230	6:56
	1240	6:47
	1250	5:64
	1260	5:60
	1270	----


CURVE VIII
II-8
$.6 Na_2O$ }
$.4 CaO$ } $3.625\ SiO_2$.
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
EUGENE DIETZGEN CO., CHICAGO.

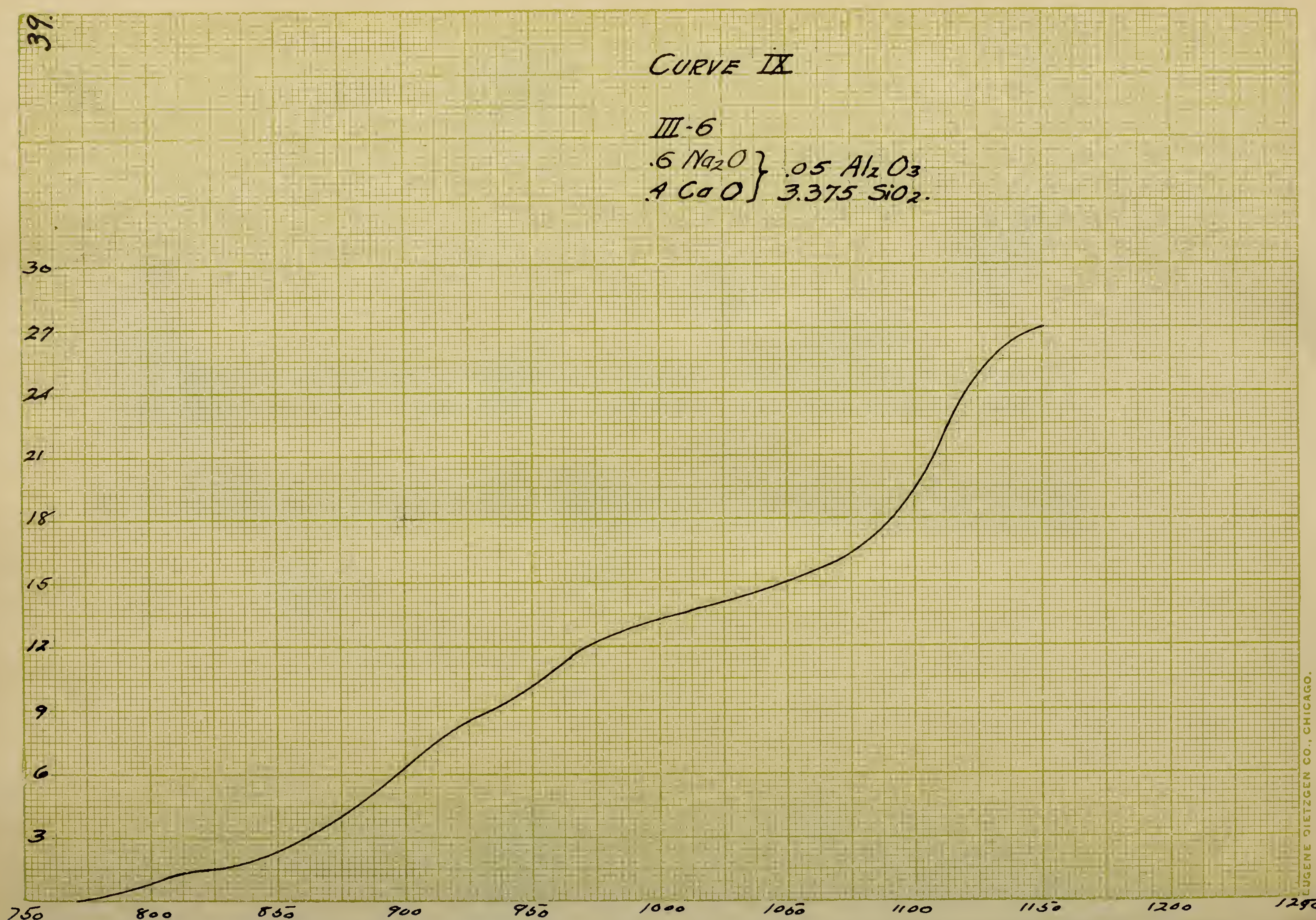
II - 9.

Time.	Temp.	Vernier.
	1140	6:76
	1150	6:75
	1160	6:74
	1170	6:73
	1180	----
	1190	6:72
	1200	6:70
	1210	6:68
	1220	6:64
	1230	6:62
	1240	6:57
	1250	5:84
	1260	4:10
	1270	3:78
	1280	----


CURVE VIII
II-9
.6 Na_2O
.4 CaO
3.75 SiO_2
3
6
9
12
15
18
21
24
27
30
800
850
900
950
1000
1050
1100
1150
1200
1250
1300
EUGENE DIETZGEN CO., CHICAGO.

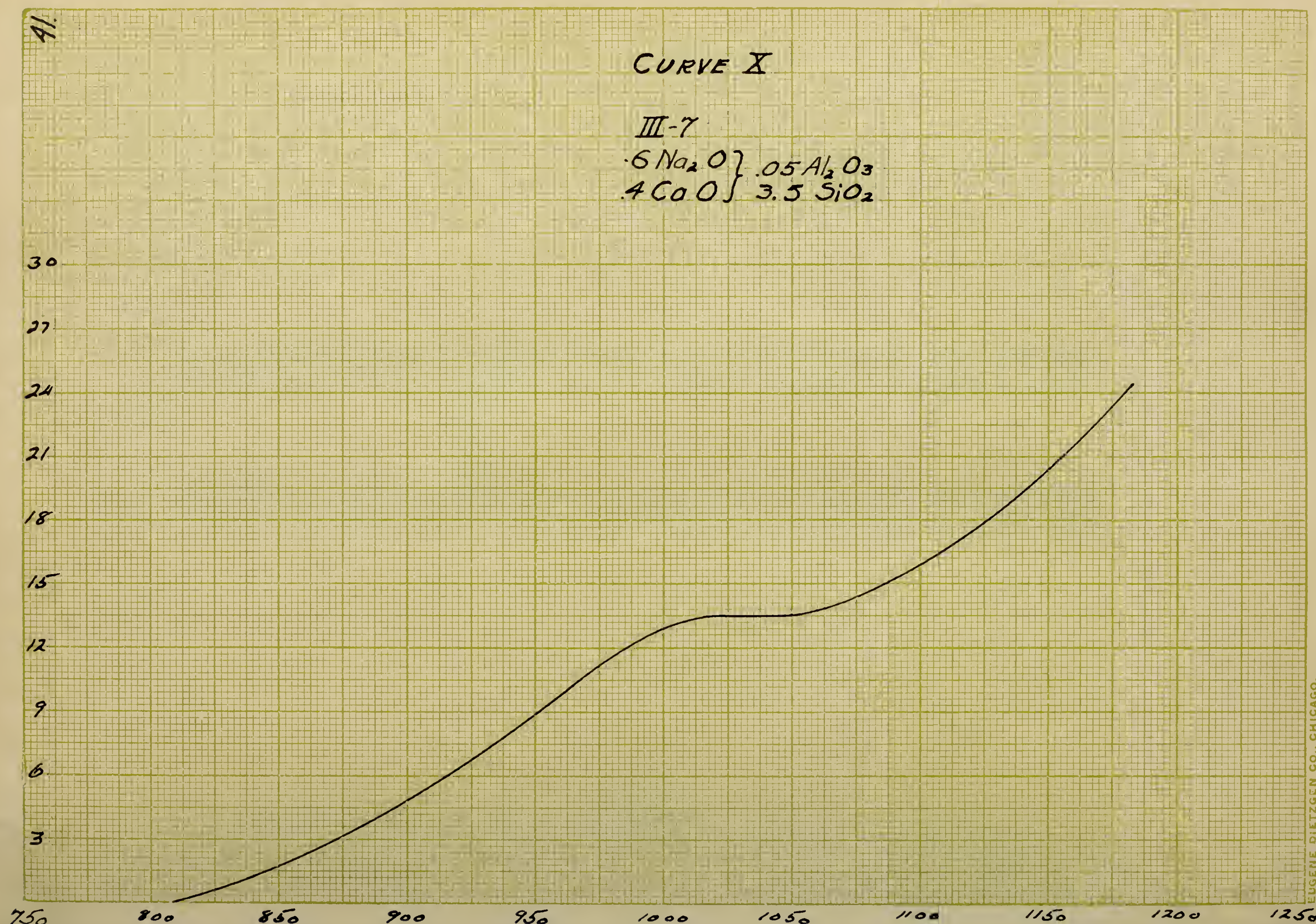
III - 6.

Time.	Temp.	Vernier.
	770	6:08
	780	6:06
	790	6:04
	800	6:01
	810	5:97
	820	5:95
	830	5:93
	840	5:90
	850	5:84
	860	5:78
	870	5:70
	880	5:64
	890	5:54
	900	5:44
	910	5:33
	920	5:27
	930	5:20
	940	5:14
	950	5:05
	960	4:96
	970	4:87
	980	4:83
	990	4:78
	1000	4:76
	1010	4:70
	1020	4:69
	1030	4:65
	1040	4:61
	1050	4:58
	1060	4:50
	1070	4:47
	1080	4:40
	1090	4:30
	1100	4:14
	1110	3:88
	1120	3:67
	1130	3:52
	1140	3:40
	1150	3:38


CURVE IX
III-6
.6 Na2O } .05 Al2O3
.4 CaO } 3.375 SiO2.
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
EUGENE DIETZGEN CO., CHICAGO.

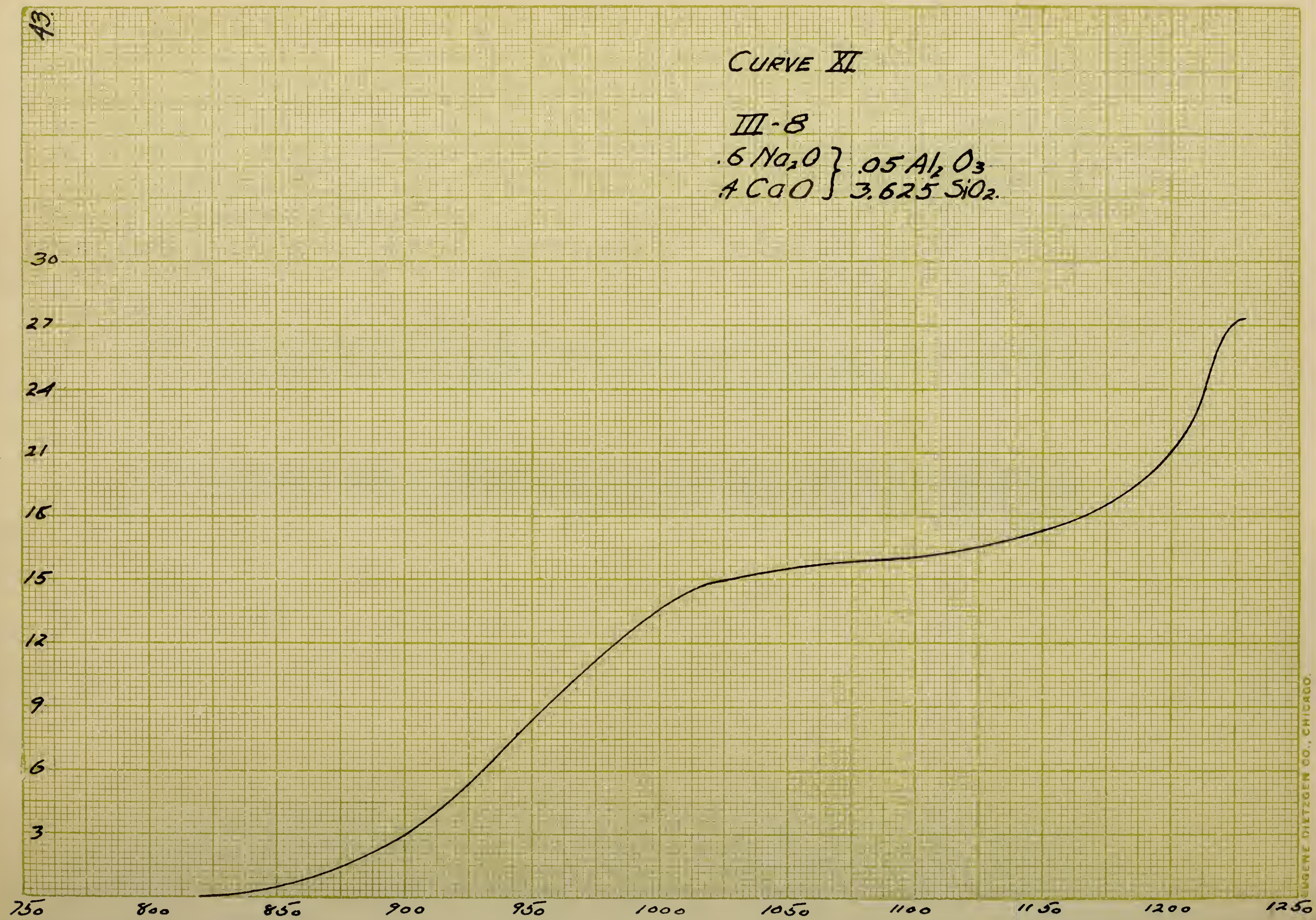
III - 7.

Time.	Temp.	Vernier.
	800	5:90
	810	5:89
	820	5:87
	830	5:84
	840	5:80
	850	5:75
	860	5:69
	870	5:63
	880	5:58
	890	5:51
	900	5:42
	910	5:35
	920	5:27
	930	5:18
	940	5:09
	950	5:00
	960	4:93
	970	4:84
	980	4:76
	990	4:69
	1000	4:60
	1010	4:58
	1020	4:57
	1030	4:55
	1040	4:54
	1050	----
	1060	4:51
	1070	4:48
	1080	4:39
	1090	4:35
	1100	4:30
	1110	4:24
	1120	4:15
	1130	4:09
	1140	4:03
	1150	3:95
	1160	3:85
	1170	3:61
	1180	3:47
	1190	3:35
	1200	----
	1210	----


CURVE X
III-7
.6 Na_2O .4 CaO } .05 Al_2O_3 3.5 SiO_2
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
EUGENE DIETZGEN CO., CHICAGO.

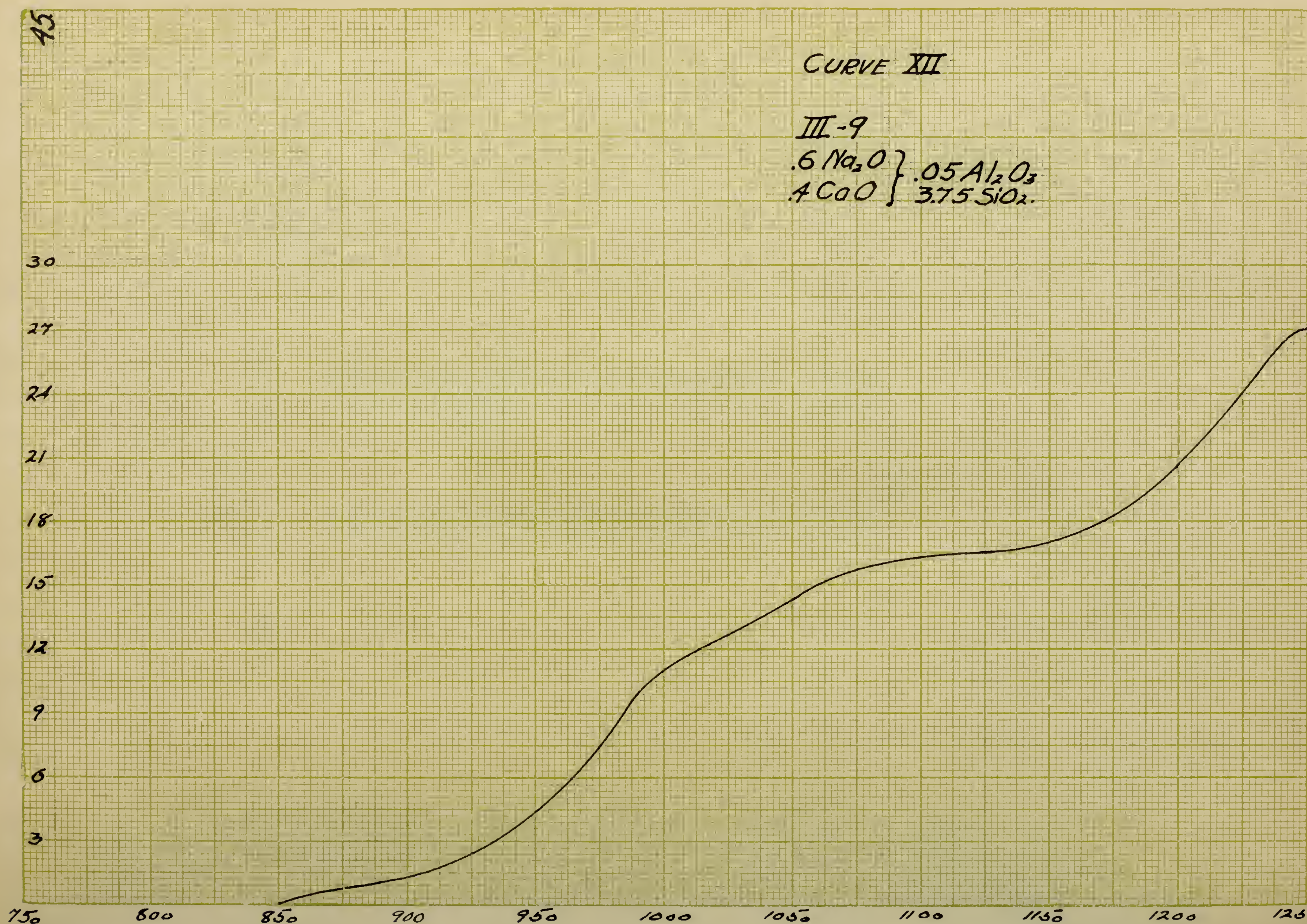
III - 8.

Time.	Temp.	Vernier.
	820	6:14
	830	6:12
	840	6:10
	850	6:08
	860	6:06
	870	6:02
	880	5:98
	890	5:92
	900	5:84
	910	5:76
	920	5:65
	930	5:53
	940	5:47
	950	5:30
	960	5:20
	970	5:10
	980	5:00
	990	4:88
	1000	4:80
	1010	4:70
	1020	4:66
	1030	4:64
	1040	4:62
	1050	4÷01
	1060	4058
	1070	4:56
	1080	----
	1090	4:54
	1100	4:50
	1110	4:48
	1120	4:47
	1130	4:45
	1140	4:43
	1150	4:40
	1160	4:37
	1170	4:32
	1180	4:23
	1190	4:14
	1200	4:00
	1210	3:80
	1220	3:47
	1230	3:40
	1240	----


CURVE XI
III-8
.6 Na₂O } .05 Al₂O₃
.4 CaO } 3.625 SiO₂.
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
EUGENE DIETZGEN CO., CHICAGO.

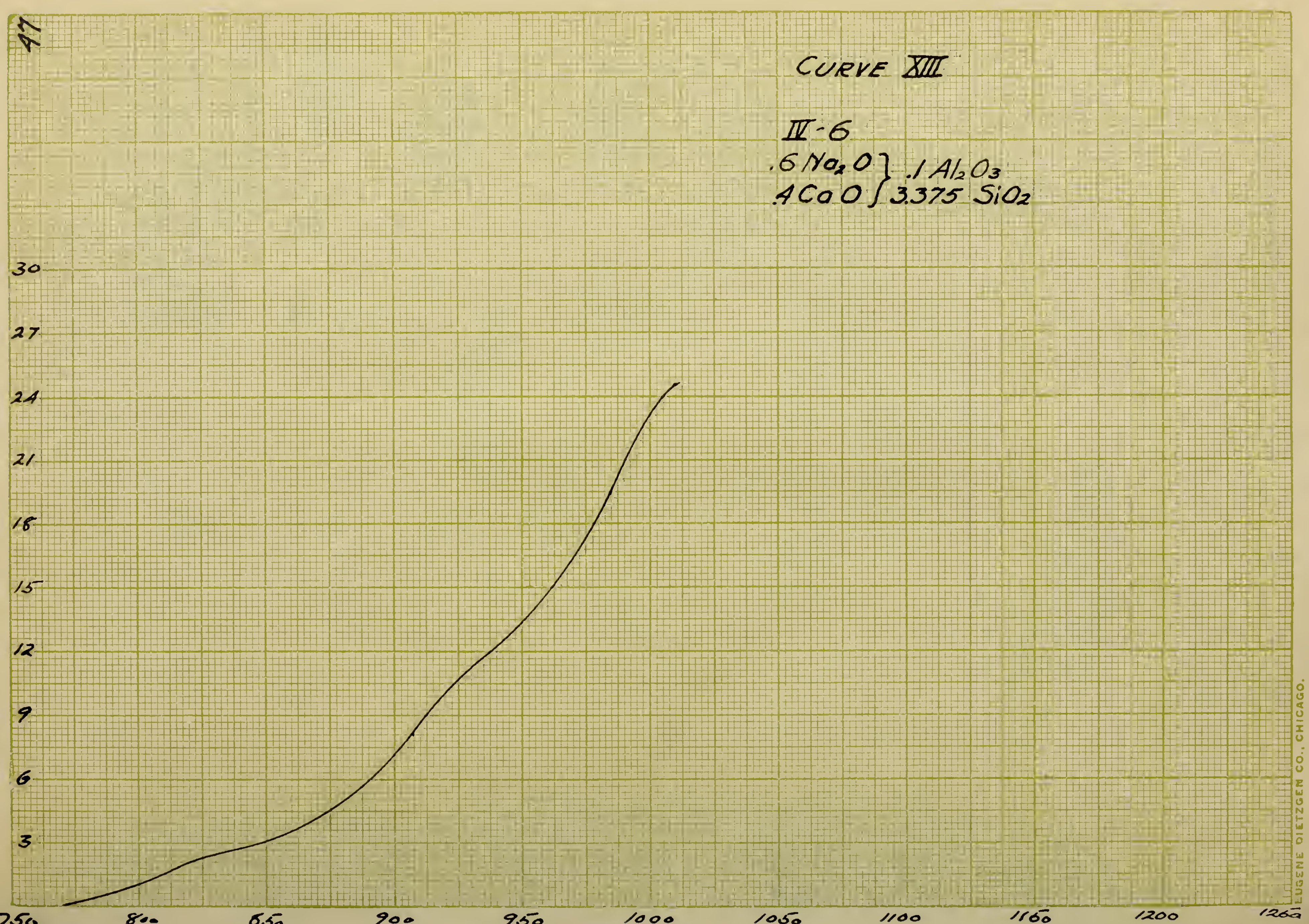
III - 9

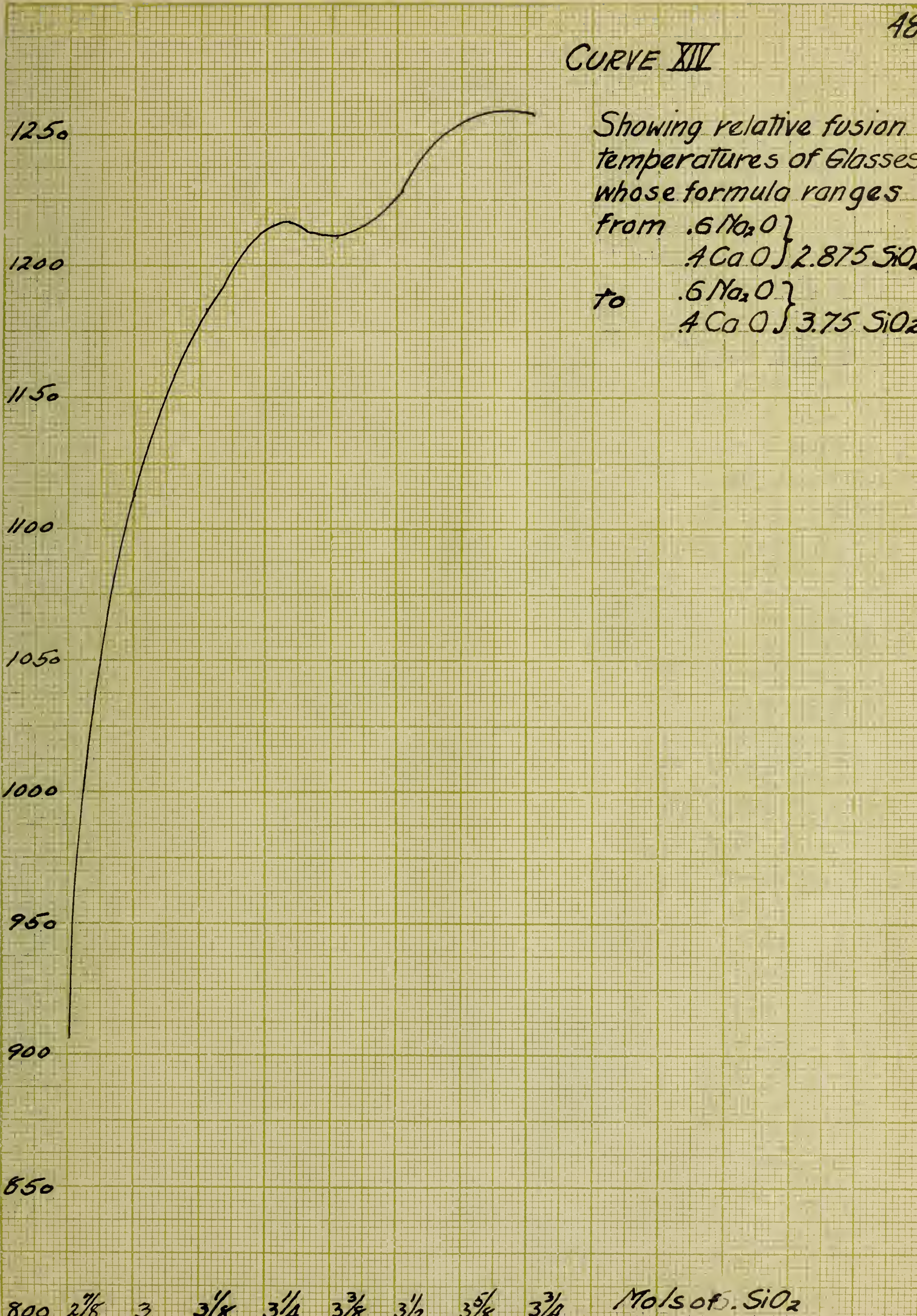
Time.	Temp.	Vernier.
	850	6:10
	860	6:07
	870	6:03
	880	6:00
	890	5:98
	900	5:95
	910	5:90
	920	----
	930	5:84
	940	5:78
	950	5:73
	960	5:58
	970	5:46
	980	5:27
	990	5:09
	1000	4:98
	1010	4:95
	1020	4:89
	1030	4:82
	1040	4:74
	1050	4:66
	1060	4:60
	1070	4:57
	1080	4:54
	1090	4:49
	1100	4:47
	1110	4:46
	1120	4:44
	1130	----
	1140	4:43
	1150	4:41
	1160	4:37
	1170	4:33
	1180	4:30
	1190	4:25
	1200	4:12
	1210	3:97
	1220	3:85
	1230	3:66
	1240	3:44
	1250	3:40

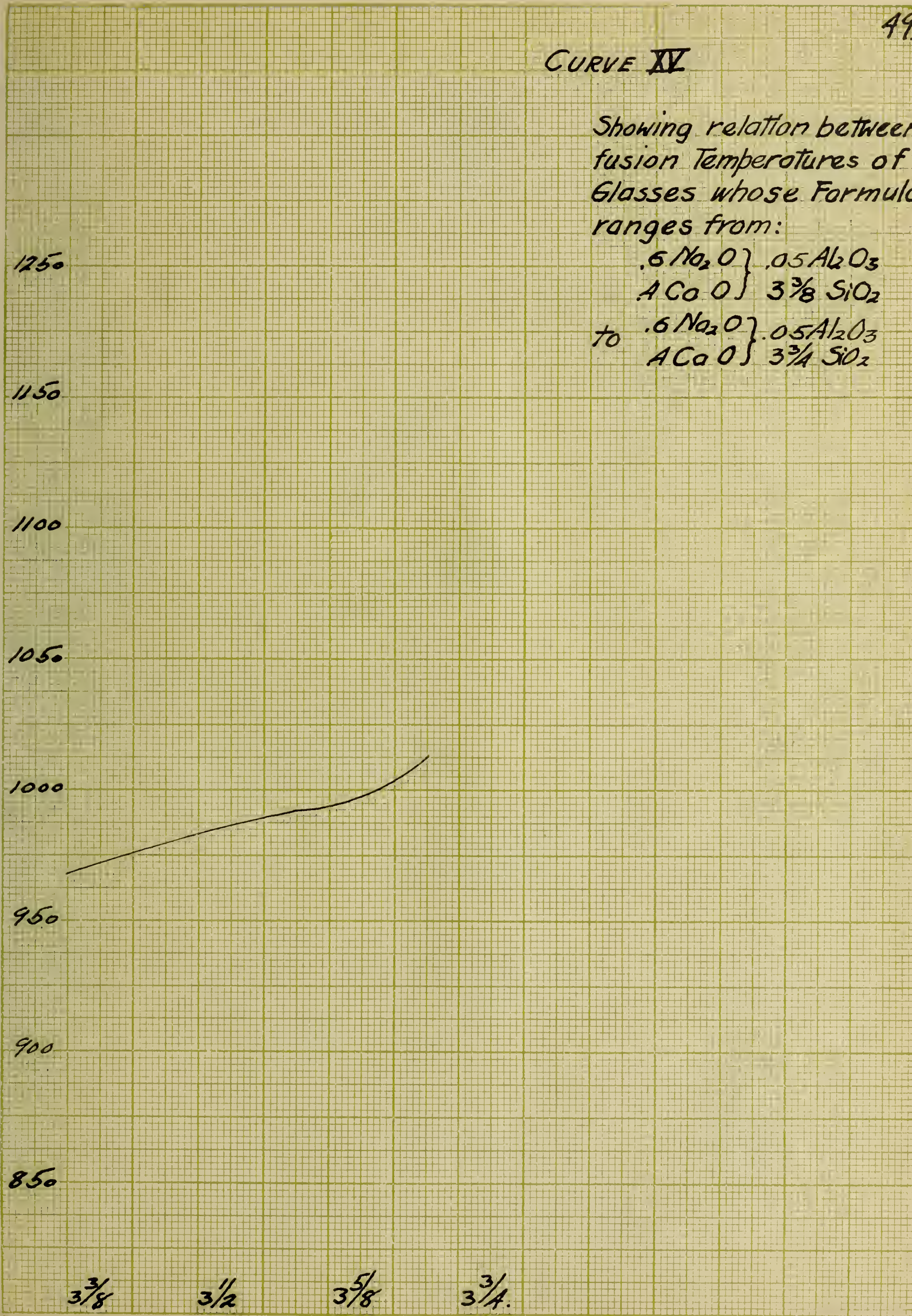

CURVE XIII
III-9
.6 Na₂O
.4 CaO
.05 Al₂O₃
3.75 SiO₂.
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250

IV - 6.

Time.	Temp.	Vernier.
	770	5:81
	780	5:80
	790	5:76
	800	5:72
	810	5:67
	820	5:63
	830	5:57
	840	5:54
	850	5:50
	860	5:45
	870	5:39
	880	5:30
	890	5:20
	900	5:08
	910	4:95
	920	4:80
	930	4:68
	940	----
	940	4:48
	960	4:37
	970	4:15
	980	3:95
	990	3:75
	1000	3:46
	1010	3:35
	1020	3:32


CURVE XIII
IV-6
.6 Na2O } .1 Al2O3
.4 CaO } 3.375 SiO2
30
27
24
21
18
15
12
9
6
3
750
800
850
900
950
1000
1050
1100
1150
1200
1250
EUGENE DIETZGEN CO., CHICAGO.


CURVE XIV
Showing relative fusion temperatures of Glasses whose formula ranges from .6 Na2O .4 CaO 2.875 SiO2 to .6 Na2O .4 CaO 3.75 SiO2
1250
1200
1150
1100
1050
1000
950
900
850
800
2 7/8
3
3 1/8
3 1/4
3 3/8
3 1/2
3 5/8
3 3/4
Mols of . SiO2

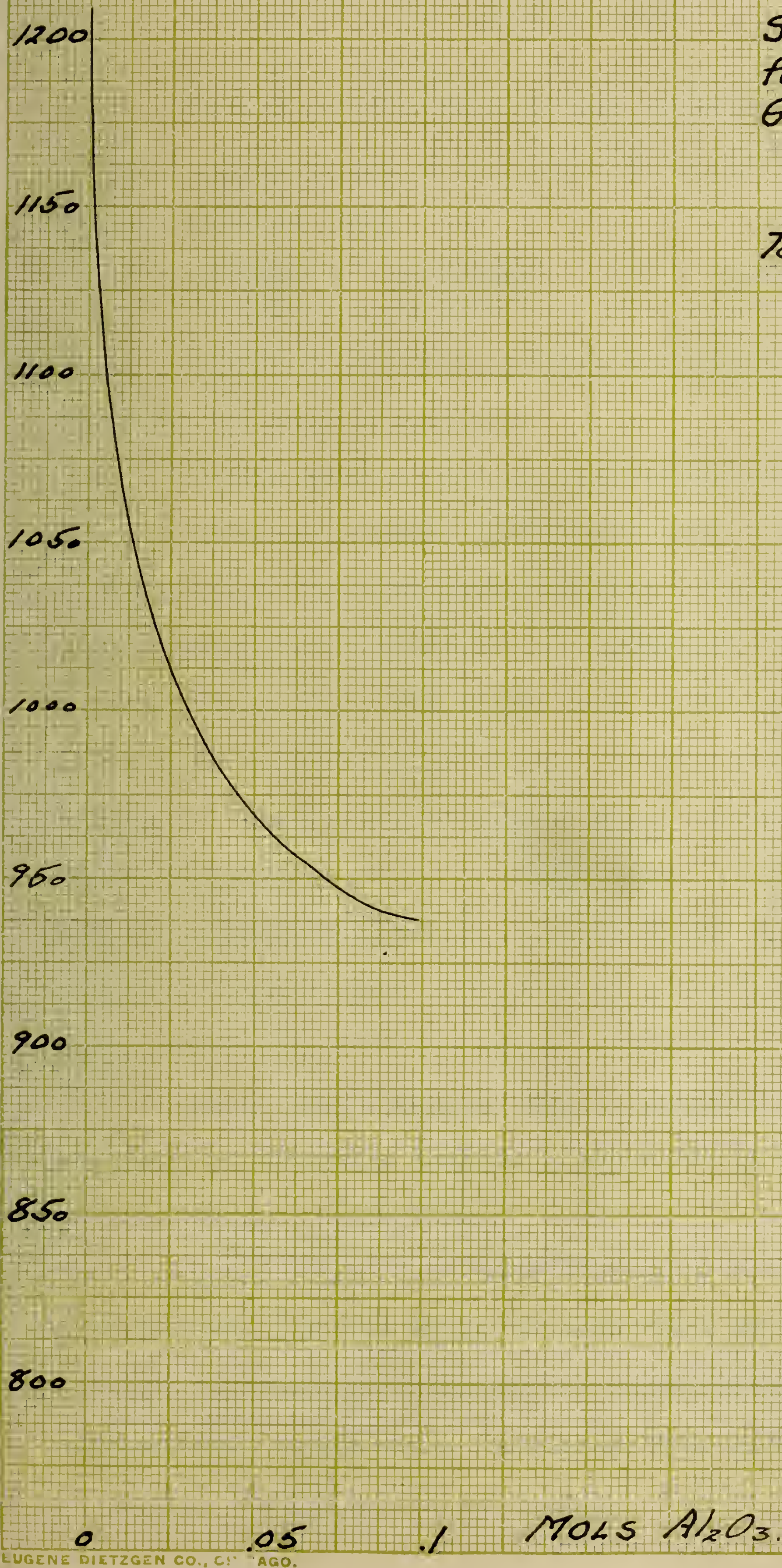

CURVE XV
Showing relation between fusion Temperatures of Glasses whose Formula ranges from:
$.6\,Na_2O$ } $.05\,Al_2O_3$
$.4\,CaO$ } $3\frac{3}{8}\,SiO_2$
to $.6\,Na_2O$ } $.05\,Al_2O_3$
$.4\,CaO$ } $3\frac{3}{4}\,SiO_2$
1250
1150
1100
1050
1000
950
900
850
$3\frac{3}{8}$
$3\frac{1}{2}$
$3\frac{5}{8}$
$3\frac{3}{4}$.

CURVE XVI

Showing relation between fusion Temperatures of Glasses ranging from:

$\left.\begin{matrix} .6\ Na_2O \\ .4\ CaO \end{matrix}\right\} \begin{matrix} 0\ Al_2O_3 \\ 3\frac{3}{8}\ SiO_2 \end{matrix}$

To $\left.\begin{matrix} .6\ Na_2O \\ .4\ CaO \end{matrix}\right\} \begin{matrix} .1\ Al_2O_3 \\ 3\frac{3}{8}\ SiO_2 \end{matrix}$



CONCLUSIONS.

From the first part of the investigation it is shown that a small amount of Al_2O_3 will prevent devitrification in glasses of formula ranging from

$$\begin{matrix} .6\ Na_2O \\ .4\ CaO \end{matrix}\Bigg) \begin{matrix} .05\ Al_2O_3 \\ 2.75\ SiO_2 \end{matrix} \quad \text{to} \quad \begin{matrix} .6\ Na_2O \\ .4\ CaO \end{matrix}\Bigg) \begin{matrix} .05\ Al_2O_3 \\ 5.73\ SiO_2 \end{matrix}$$

while glasses of the same composition without Al_2O_3 will devitrify under the same conditions.

In the second part of the investigation curves 1 to 13 inclusive show an increase in temperature of fusion with increase in SiO_2 and a decrease with addition ot Al_2O_3 but an increase in viscosity with the addition of Al_2O_3. The rod begins to sink at a lower temperature but sinks more slowly in glasses containing Al_2O_3 than those without Al_2O_3. Curve 14 shows a relative increase in temperature of fusion with increase of SiO_2. Curve 15 shows relative increase in temperature of fusion with increase in SiO_2 in glasses containing Al_2O_3. Curve 16 shows relative decrease in temperature of fusion of glasses varying from 0 to .1 Al_2O_3 other constituents being constant.

From the foregoing work it appears that Al_2O_3 can be employed to overcome devitrification which at the same time lowers the softening temperature.

Since Al_2O_3 increases viscosity or prolongs the softening temperature, its use would be desirable in that it gives a longer plastic interval for shaping the glass without liability of devitrification. Since Al_2O_3 increases viscosity, its use would tend to retard clarification or fining.

Although the Al_2O_3 as herein used was in the form of the hydroxide, its introduction into glass can be accomplished very inexpensively in the form of kaolin or feldspar.

That Al_2O_3 lowers the softening temperature of glasses when used in amounts not exceeding 0.1 Mols as herein shown is contrary to the erroneous belief of practical glass makers.